Pesticides in marine microorganisms.

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Introduction.

This report deals with results obtained from samples taken on the cruises in the North Sea during June, July, September and October 1972. These samples are listed in Tables Ia, Ib, Ic, (place, date and time of sampling).
Sampling was done using a plankton net of 250 u. As a rule ± 50 g of wet weight sample was taken, 40 g of this sample was analysed.

The procedure used was the same as discribed in a previous report(1), Extraction and clean-up was worked out for samples with a low fat content. (Direct extraction with hexane, clean-up on a standardized florisil column, elution in two fractions : hexane and hexane/ether 1/1.) These two fractions were analysed gaschromatographically on a Hewlett-Packard 5750 G with a Ni^{63} electron capture detector.

(1) Pesticides in marine microorganisms.
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identification place	date	time of sampling	dry organic matter present in 40 g wet plankton, expressed in g.
M01	26-6-72	15.30	1.01
M02	3-7-72	15.30	
M03	4-7-72	10.30	0.70
M04	4-7-72	15.00	1.30
M05	30-6-72	10.00	0.81
M06	7-7-72	10.00	0.82
M07	7-7-72	14.30	0.68
M08	10-7-72	15.30	1.31
M09	11-7-72	10.00	
M10	11-7-72	15.30	
M11	13-7-72	15.15	
M12	13-7-72	10.30	0.46
M13	14-7-72	10.00	
M14	12-7-72	15.30	
M15	12-7-72	10.00	
M16	29-6-72	15.30	0.74
M17	6-7-72	10.30	
M18	6-7-72	15.30	0.68
M19	5-7-72	15.00	
M20	5-7-72	10.00	0.75
M21	29-6-72	10.30	0.77
M22	28-6-72	15.30	0.72
M23	28-6-72	10.30	0.83
M24	27-6-72	15.30	0.62
M25	27-6-72	10.30	0.79

Table Ia. Samples taken in June, July 1972.

identification place	date	time of sampling	dry organic matter present in 40 g wet plankton, expressed in g
1097	6-9-72	16.30	0.74
M01	6-9-72	12.00	0.47
1344	25-9-72	17.00	0.49
1348	25-9-72	13.30	0.42
1352	11-9-72	15.00	0.62
1358	11-9-72	19.00	
1486	28-9-72	15.30	0.81
M61	14-9-72	14.00	0.32
1634	14-9-72	09.00	0.71
M59	28-9-72	09.30	0.24
1699	8-9-72	13.30	0.58
1778	8-9-72	10.00	0.65
M67	7-9-72	14.00	0.41
1930	7-9-72	09.30	0.74
2552	28-9-72	13.00	0.85
1693	13-9-72	13.00	
M65	13-9-72	09.00	
2001	12-9-72	13.30	
M72	12-9-72	10.00	
2689	27-9-72	15.30	
M16	27-9-72	10.00	0.38
1993	26-9-72	12.15	0.68
M22	26-9-72	10.00	0.99
2841	27-9-72	12.00	0.59

Table Ib. Samples taken in September 1972.

identification place	date	time of sampling	dry organic matter present in 40 g wet plankton, expressed in g.
M01	11-10-72	15.30	0.31
M02	12-10-72	10.40	0.74
M03	12-10-72	12.50	0.74
M04	12-10-72	16.10	
M05	10-10-72	13.25	0.30
M06	10-10-72	10.25	0.67
M07	9-10-72	16.15	0.80
M08	19-10-72	11.30	0.88
M09	16-10-72	14.00	0.48
M10	13-10-72	09.40	
M14	19-10-72	18.30	0.51
M15	19-10-72	15.00	0.44
M23	18-10-72	09.30	0.78
M25	17-10-72	10.30	
M25	17-10-72	15.30	0.39

Table Ic. Samples taken in October 1972

Operating conditions

Column :

First column : 6 ft x 4 mm Ø, 3 % SE-30 as stationary phase on diatoport 60-80 mesh.

Second column : 3 % QF-1 on chromosorb W.

Carrier : He (flow : 40 ml/minute).

Purge : CH_4-Ar (flow : 100/ml minute).

Oven temperature : 216° C.

Detector temperature : 265° C.

Electrometer range x attenuation = 10^2 x 4

Table II gives the minimal detection limit, in organic matter as substrate (expressed in µg/gram), and the R_t-value of the different pesticides.

Pesticide	R_t-value	Minimal detection amount (g)	Minimal amount (µg) for being detected in 1 g dry organic matter
Lindane	0,28	5×10^{-11}	0,01
Heptachlor	0,46	5×10^{-11}	0,01
Aldrin	0,56	3×10^{-11}	0,006
pp'DDE	1,00	10×10^{-11}	0,02
Dieldrin	1,00	10×10^{-11}	0,02
Endrin	1,14	5×10^{-11}	0,01
pp'TDE	1,24	10×10^{-11}	0,02
pp'DDT	1,61	10×10^{-11}	0,02
Methoxychlor	2,25	10×10^{-11}	0,02

Qualitative interpretation of the gaschromatographic results was worked out on basis of R_t - values ($R_{t\ dieldrin} = 1$).

Confirmation was done on the second column on connection with thin-layer chromatography.

The quantitative determination for the organochlorine insecticides was made against standard pesticide solutions within the lineair range of the detector.

For the determination of the PCB's, each peak in the hexane eluant has been given a letter (Table III).
With the peak height rapport g/h, i/h the PCB's are identified as Aroclor 1254 or 1260 (Table IV).
The standard PCB's 1254 and 1260 are used for quantitative determination.

Table III

Relative R_F values of PCB-mixtures Aroclor 1232, 1242, 1248, 1254, 1260, 1262 (16,6 ng/ µl) on SE-30, after elution from a florisil column.

a	0.41	g	1.44
b	0.52	h	1.54
c	0.71	i	1.68
d	0.86	j	1.92
e	1.00	k	2.19
f	1.24	l	2.58

Table IV

Peak height rapport of Aroclor-mixture (1254,1260)

	g/h	i/h
Aroclor 1254	3.5	3
Aroclor 1260	2.4	1.8

Table V gives the results of the samples of June and July 1972. Table VI the results of the samples of September and Table VII these of October 1972. The amounts are expressed in ppm (µg pesticide/g dry organic matter weight).

In Fig. I, II and III, the total amount of organochlorine insecticides (heptachlor, heptachlorepoxide, DDE, DDT, TDE, dieldrin and endrin), the PCB's and the amount of dry organic matter present in 40 g wet sample are localized on the sampling places.

Identification sample	Hepta-chlor	Heptachlor-epoxide	DDE	Dieldrin	Endrin	TDE	DDT	Methoxy-chlor	Aroclors 1254	Aroclors 1260	Number of unknown peaks (Hex. el.)	Number of unknown peaks (Hex.eth.ek.)
M01 26-6-72												
M03 4-7-72			0.035			t			traces		1	
M04 4-7-72			0.023						traces		3	
M05 30-6-72				0.026		0.030					3	
M06 7-7-72				0.036	t	0.041			0.240		9	
M07 7-7-72												
M08 10-7-72		t		t	t	t	t					
M12 13-7-72				t							1	
M16 29-6-72				t							1	
M18 6-7-72												
M20 5-7-72				t					traces			
M21 29-6-72				0.040	0.026	0.031					1	
M22 28-6-72									traces		1	
M23 28-6-72						0.096			traces		2	
M24 27-6-72									traces			
M25 27-8-72									traces		1	

Table V : June-July 1972. Figures in ppm (µg pesticide in 1 g dry organic matter weight

x = means that the considered pesticide was found in the sample
t = traces

Identification sample	Hepta-chlor	Heptachlor-epoxide	DDE	Dieldrin	Endrin	TDE	DDT	Methoxy-chlor	Aroclors 1254	Aroclors 1260	Number of unknown peaks (Hex. el.)	Number of unknown peaks (Hex. Eth. el.)
MO1 11-10-72			0.184				x	0.040			2	4
MO2 12-10-72		t	0.061		t				traces			
MO3 12-10-72	t		0.030									4
MO5 10-10-72		0.030	0.490		t				traces			
MO6 10-10-72			0.053	0.033	0.044		t	x	0.250			6
MO7 9-10-72			0.024		t					0.200		1
MO8 19-10-72			0.010	t					traces			
MO9 16-10-72				x					traces			8
M14 19-10-72			0.025	0.031					traces			
M15 19-10-72												
M23 18-10-72			0.020		t				x			
M25 17-10-72										2.000		1

Table 7 : October 1972. Figures in ppm (µg pesticide in 1 g dry organic matter weight.

x means that the considered pesticide was found in the sample

t means traces

Identification sample	Hepta-chlor	Heptachlor-epoxide	DDE	Dieldrin	Endrin	TDE	DDT	Metoxy-chlor	Aroclors 1254	Aroclors 1260	Number of unknown peaks (Hex. el.)	Number of unknown peaks (Hex.Eth.el.)
1097 6-9-72				t	t				traces			2
M01 6-9-72				t					traces			
1344 25-9-72									traces			2
1348 25-9-72			x			x						1
1352 11-9-72		t		t		t	t					4
1358 11-9-72												
1486 28-9-72				0.020					traces			1
M61 14-9-72	0.056		0.050	0.050			x	x	traces			3
1634 14-9-72								x				1
M59 28-9-72				x								
1699 8-9-72				t					traces			1
1778 8-9-72			t	t				x	traces			
M67 7-9-72		x		0.036		x		x	traces			
1930 7-9-72				0.025		x			traces			
2252 28-9-72		0.050	0.100	0.100	0.170			2.000	traces			
1693 13-9-72				t		t	t					2
M65 13-9-72									t			2
2001 12-9-72			0.035		0.035		x					
M72 12-9-72		0.043					x					
M16 27-9-72				t					traces			
1993 26-9-72		0.006							traces			1
2841 27-9-72				0.038	0.043		x	t		1.260		1

Table 6 : September 1972. Figures in ppm (µg pesticide in 1 g dry organic matter weight.)

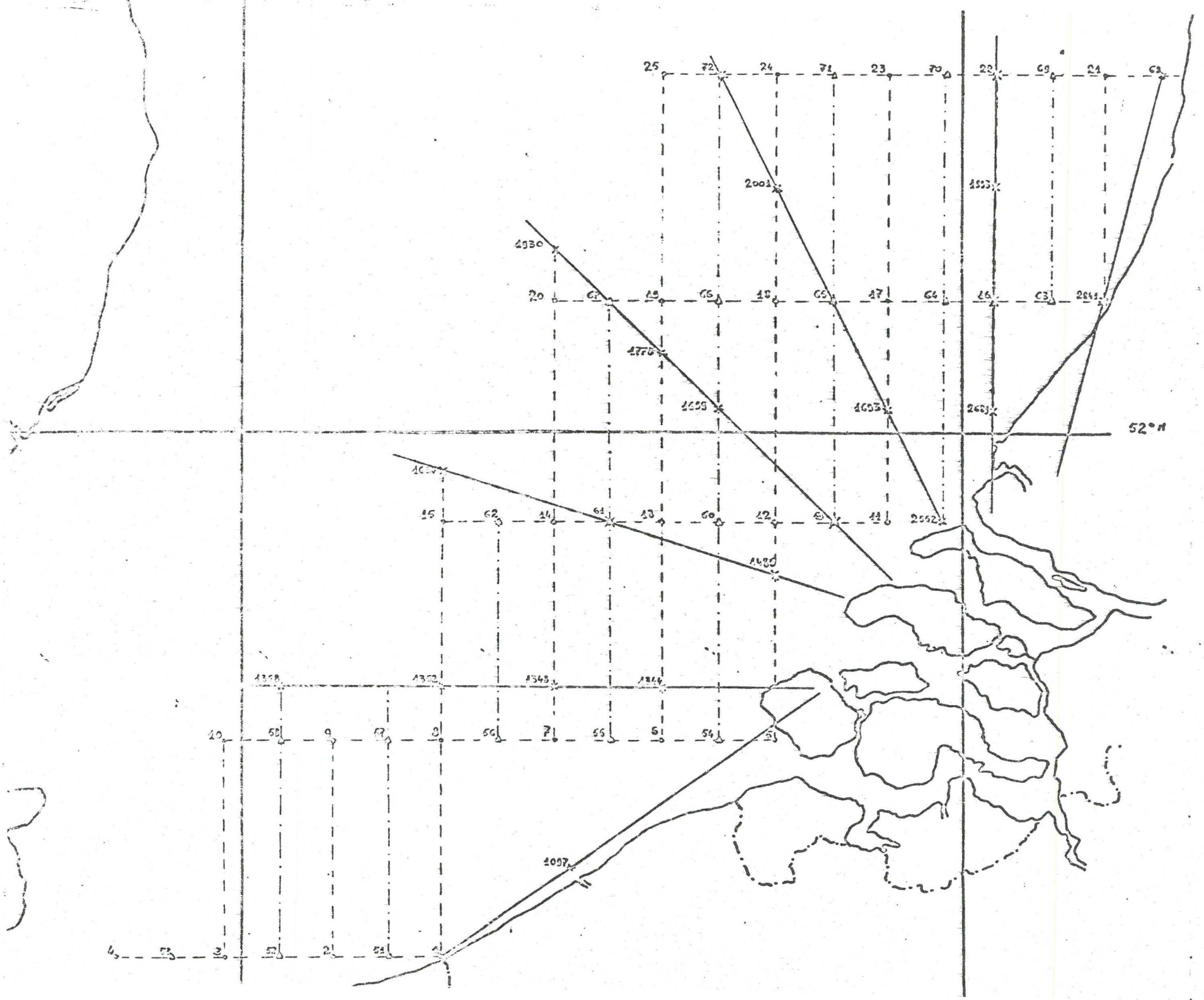
x means that the considered pesticide was found in the sample

t means traces

Discussions

1. The distribution-pattern of the total amount of the pesticide and the PCB's in microorganisms as given in Fig. I, II, III shows the highest concentration in the coastal area. (M01, M02, M05, M06, 2552, 2841).
   Certain other points have relative high amounts e.g. M 61, M 67, M 25).
   In a relative important number of samples the figures are negative due to the insufficient amount of sample or concentration below the sensitivity of the method.

2. None of the BHC's are reported because of difficulties in quantitative interpretation (interferences).
   Nevertheless they are present in all samples reported, in quantities not exceeding 0,01 ppm.


52°N

JUNE = JULY 1972.

1 cm height represents 1 g dry organic matter from 40 g wet plankton.

1 cm height represents 0.5 ug aroclors, present in 1 g dry organic matter.

1 cm height expresses 0.1 ug total amount of pesticide found in 1 g dry organic matter.

△ unsufficient plankton sampling.

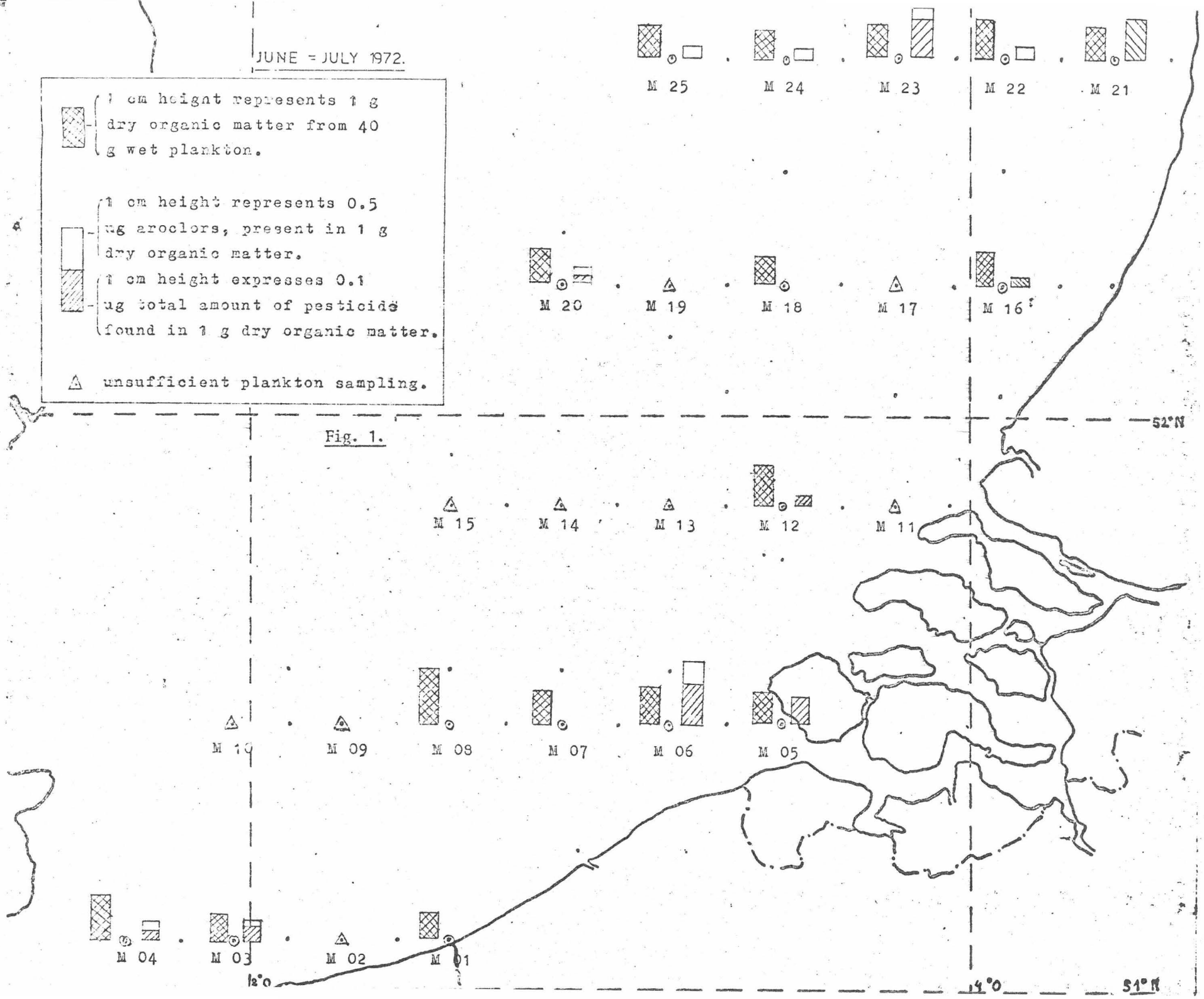


Fig. 1.

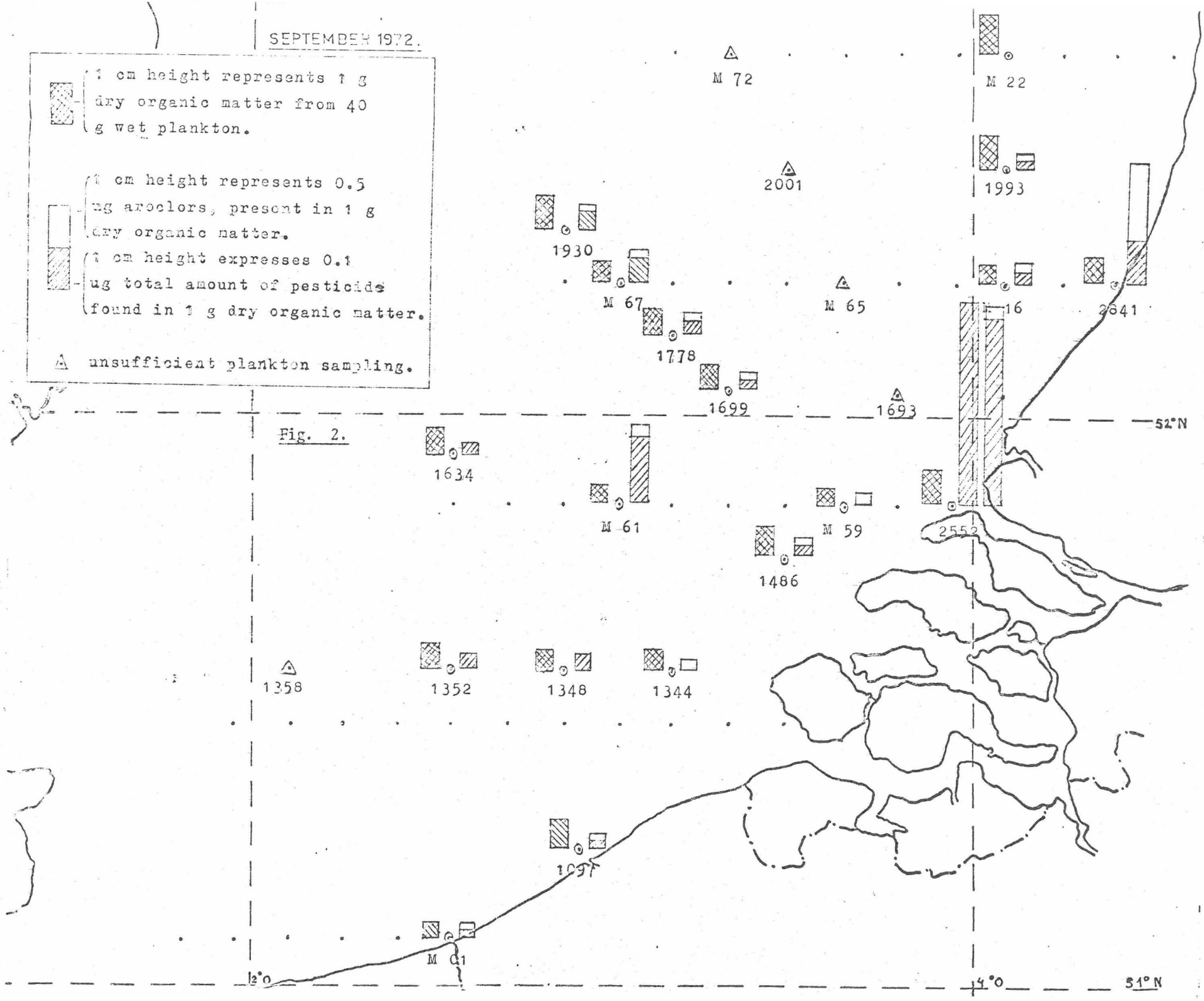

SEPTEMBER 1972.
1 cm height represents 1 g dry organic matter from 40 g wet plankton.
1 cm height represents 0.5 ng aroclors, present in 1 g dry organic matter.
1 cm height expresses 0.1 ug total amount of pesticids found in 1 g dry organic matter.
unsufficient plankton sampling.
M 72
M 22
2001
1993
1930
M 67
M 65
16
2641
1778
1699
1693
52°N
1634
M 61
M 59
2552
1486
1358
1352
1348
1344
M 01
2°0
4°0
51°N

Fig. 2.

1 cm height represents 1 g dry organic matter from 40 g wet plankton.

1 cm height represents 0.5 ug aroclors, present in 1 g dry organic matter.

1 cm height expresses 0.1 ug total amount of pesticide found in 1 g dry organic matter.

△ unsufficient plankton sampling.

Fig. 3.